



Water delignification by advanced oxidation processes: Homogeneous and heterogeneous Fenton and H₂O₂ photo-assisted reactions

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ARTICLE INFO

Article history:

Received 18 March 2008

Received in revised form 12 June 2008

Accepted 18 June 2008

Available online 24 June 2008

Keywords:

Hydrogen peroxide

Lignin

Catalysis

Oxidation

FeZSM-5

ABSTRACT

The oxidation of lignin in synthetic aqueous solutions as well as in the biologically treated pulp-and-paper mill wastewater with hydrogen peroxide was studied in various methods: hydrogen peroxide UV-photolysis, homogeneous, heterogeneous and UV-assisted heterogeneous Fenton reactions, catalysed by FeZSM-5 zeolite. Contrasting the low-molecular organic contaminants, the oxidation of lignin in aqueous solutions was drastically slowed down in presence of heterogeneous FeZSM-5 zeolite, showing the superior performance of acidic homogeneous Fenton and hydrogen peroxide photolysis. This is explained by steric hindrance in oxidation of lignin with OH radicals on the catalyst surface and possible deactivation of lignin molecules adsorbed on the zeolite. The hydrogen peroxide photolysis among the studied delignification methods appeared to be the most efficient one in a wide range of pH.

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1. Introduction

Lignin is a cell wall constituent of the majority of terrestrial plants, which provides plant strength and resistance to microbial degradation. The lignin molecule is an irregular tri-dimensional polymer composed of aromatic, mostly phenolic units. Lignin in nature occupies the second place by its abundance among natural high-molecular compounds after carbohydrates. Firwood and foliferous wood contain 28–30% and 18–24% of lignin, respectively [1]. In pulp mills lignin is separated from fibres to be disposed with wastewaters containing lignin as the main constituent of chemical oxygen demand (COD) and colour. Having lifetime under natural conditions as long as 200 days, lignin is even more problematic due to formation of toxic by-products during its decomposition such as phenols, aldehydes, ketones, methanol and carboxylic acids affecting the aqueous ecosystem [2].

Advanced oxidation processes (AOPs) utilising oxidation potential of OH radical formed under ambient conditions were being studied for water delignification for the last few years: photocatalytic oxidation [3–5], hydrogen peroxide photo-assisted processes [6], homogeneous Fenton and photo-Fenton systems [7], ozonation and UV-assisted ozonation [6,8,9]. This paper presents experimental results in oxidation of lignin using heterogeneous

Fenton and photo-Fenton reactions. The results were compared with homogeneous Fenton and H₂O₂/UV treatment. Solid state FeZSM-5 zeolite was shown to be active heterogeneous catalyst in oxidation of various substances, such as phenols [10], carboxylic acids [11] and 1,1-dimethylhydrazine [12] with hydrogen peroxide. The efficiency in utilisation of hydrogen peroxide in heterogeneous Fenton reaction was shown to be superior over that in homogeneous system, which was explained by concentrating effect of low-molecular compounds on the zeolite surface [13]. The efficiency of FeZSM-5/H₂O₂ system, however, is not known in respect of oxidation of high-molecular lignin. The present paper discusses the performance of H₂O₂/UV, Fe(NO₃)₃/H₂O₂, FeZSM-5/H₂O₂ and FeZSM-5/H₂O₂/UV in aqueous oxidation of lignin in synthetic solutions, and in the wastewater from a pulp-and-paper mill.

2. Experimental

2.1. Materials

Alkali lignin with mean M_w = 28,000, iron(III) nitrate nonahydrate and titanyl sulphate were supplied by Sigma–Aldrich, 30% hydrogen peroxide aqueous solution, sodium hydroxide, 25% hydrochloric acid, cobalt(II) chloride hexahydrate, and concentrated sulphuric acid were obtained from Merck and used without additional treatment. The synthesis of FeZSM-5 catalyst was described in [14]. Subsequent to hydrothermal treatment with

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$\text{Fe}(\text{NO}_3)_3$, Fe-containing catalyst was activated as described elsewhere [15]. The XRD analysis showed a typical ZSM-5 zeolite structure of the catalyst. The catalyst was analysed for its elemental composition with ICP-OES and contained 2.4 wt.% Fe, 0.13 wt.% Al and 0.008 wt.% Na. Nitrogen adsorption at 77 K showed that the BET surface area of the catalyst was $343.4 \text{ m}^2 \text{ g}^{-1}$, external surface area was $53.72 \text{ m}^2 \text{ g}^{-1}$ and mesopore volume was $0.092 \text{ cm}^3 \text{ g}^{-1}$. The biologically treated wastewater was taken from the Kaukas paper mill (UPM Kymmene, Finland).

2.2. Adsorption tests

The adsorption batch tests were carried out at 25°C for 2 h in lignin aqueous solutions with its initial concentration from 50 to 1000 mg L^{-1} . The adsorbent mass (g) to solution volume (mL) ratio was 1:62.5. The solution pH was adjusted with 1-M solutions of HCl or NaOH.

2.3. Catalytic and photolytic tests

200-mL batch reactors (evaporation dishes) agitated with magnetic stirrers and thermostatted at 25°C with an inner diameter of 70 mm, aperture open for irradiation $19 \text{ m}^2/\text{m}^3$, were used in oxidation experiments. The initial lignin concentration was from 50 to 650 mg L^{-1} , the initial H_2O_2 concentration was from 0.25 to 3 M, FeZSM-5 concentration was 16 g L^{-1} in heterogeneous Fenton system, $\text{Fe}(\text{NO}_3)_3$ concentration was 5 mM in homogeneous Fenton system. The concentrations of FeZSM-5 and $\text{Fe}(\text{NO}_3)_3$ were thoroughly selected previously in [14] based on maximum activities in H_2O_2 decomposition. To avoid complications caused by water evaporation, so called “reference” reactor exposed to identical experimental conditions was used parallel with the “active” one. The reference reactor contained all components of the reaction mixture except hydrogen peroxide. Photo-assisted experiments were carried out using a low pressure mercury UV lamp Philips G15T8 with maximum irradiation at 254 nm, placed horizontally over the reactor as was described elsewhere [3]. The incident irradiance was measured by optical radiometer UVX at a distance equal to the level of the free surface of the reactor and was 2.3 mW cm^{-2} . 100-mL samples of lignin-containing wastewater were used in the experiments.

The initial oxidation rate for lignin, $\text{mg L}^{-1} \text{ s}^{-1}$, was determined as the rate of decrease in lignin concentration in 5 to 30 min from the start of the reaction. To avoid the interference of lignin adsorption on the zeolite FeZSM-5 surface, the samples for analysis were adjusted to pH 11.0, at which lignin adsorption on zeolite was found to be negligible, after that the samples were filtrated from the zeolite. The initial lignin mineralization rate, $\text{mg L}^{-1} \text{ s}^{-1}$, was determined as the rate of decrease in total organic carbon (TOC) concentration in 5–30 min from the start of the reaction. Before the TOC analysis the solutions were adjusted to pH 5 to avoid additional CO_2 dissolving from air.

2.4. Analytical tests

The lignin elemental composition was determined using automatic CHNS-analyser EURO EA 3000. The content of carbon, hydrogen and oxygen was 56.86, 4.44, and 48.70 wt.% respectively.

Hach DR/200 spectrophotometer was used to determine concentrations of lignin (method 8193 with sodium molybdate and sodium tungstate(VI) forming blue-coloured intermediates with lignin measured at 700 nm, adapted from [16,17]), hydrogen peroxide (with titanil sulphate at $\lambda = 405 \text{ nm}$ for $\text{H}_2\text{O}_2/\text{TiOSO}_4$ absorption band, $\varepsilon = 700 \text{ M}^{-1} \text{ cm}^{-1}$ [18]), chemical oxygen demand (method 8000 with potassium dichromate and sulphuric acid),

turbidity (measured at 450 nm in FTUs) and colour (at 455 nm). The standard method 8193 for lignin determination does not allow precise distinguishing hydroxylated aromatic compounds, of which lignin is composed of. However, the commercial reagent called “lignin” is an irregular polymer, a mixture of different polymeric aromatic compounds. Natural lignin may be an even more complex substance. Therefore, the lignin oxidation rate determined in this paper was referred to the oxidation rate of integrated composition of “lignin-like” compounds, sensitive towards the reaction used in the standard method. The reaction resulting in elimination of lignin-like compounds is considered as the delignification. The rate of lignin mineralization and the mineralization degree were determined from the TOC concentration changes measured with the Shimadzu TOC analyser.

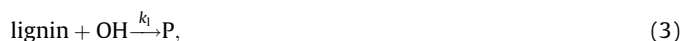
To avoid the interference of hydrogen peroxide with the lignin concentration and COD measurements, H_2O_2 was removed from the samples before analyses by adding 1 M NaOH and 10 mM CoCl_2 as a catalyst to the sample in 1:10 volumetric ratio: hydrogen peroxide decomposed fast in alkaline media without further oxidation of lignin, which was proved with special tests using 1 M H_2O_2 at initial lignin concentrations up to 60 mg L^{-1} .

3. Results and discussion

3.1. Photo-assisted lignin oxidation with hydrogen peroxide

Lignin solutions were resistant to UV-light, when no H_2O_2 was added. With added hydrogen peroxide under UV-radiation, lignin yielded to oxidation, which may be simplistically described by the following reactions.

Hydrogen peroxide under UV-radiation yields two OH radicals. A part of these reacts with H_2O_2 , when another with lignin:



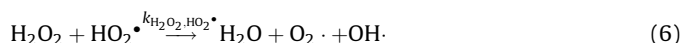
where P summarizes the products of delignification reaction. Two more reactions of OH radical loss may be taken into account [19]:



and



Reaction of HO_2^\bullet radical with hydrogen peroxide should be also considered:



The initial OH radical's production rate (r_1^0) can be modelled by the following equation:

$$r_1^0 = 2 \cdot k_{\text{a},\text{H}_2\text{O}_2}(\lambda) \cdot \Phi_{\text{OH}}(\lambda) \cdot [\text{H}_2\text{O}_2]_0, \quad (7)$$

where $k_{\text{a},\text{H}_2\text{O}_2}(\lambda)$ is the specific rate of absorption of photons of wavelength $\lambda = 254 \text{ nm}$ by a mole of hydrogen peroxide, Einstein $\text{mol}^{-1} \text{ s}^{-1}$ (Eq. (8)), accounting that this wavelength is also absorbed by lignin:

$$k_{\text{a},\text{H}_2\text{O}_2}(\lambda) = \frac{F_p(\lambda) \cdot \varepsilon_{\text{H}_2\text{O}_2}(\lambda) \cdot [1 - 10^{-(\varepsilon_{\text{lignin}}(\lambda) \cdot [\text{lignin}]_0 + \varepsilon_{\text{H}_2\text{O}_2}(\lambda) \cdot [\text{H}_2\text{O}_2]_0) \cdot z}]}{(\varepsilon_{\text{lignin}}(\lambda) \cdot [\text{lignin}]_0 + \varepsilon_{\text{H}_2\text{O}_2}(\lambda) \cdot [\text{H}_2\text{O}_2]_0) \cdot z}, \quad (8)$$

$\Phi_{\text{OH}}(\lambda)$ is the quantum yield of H_2O_2 photolysis giving two OH radicals, mol Einstein^{-1} (taken as 1.0 for the wavelengths below 300 nm [20]), $E_p^0(\lambda)$ is the incident photon flux at 254 nm, $10^{-3} \text{ Einstein cm}^{-2} \text{ s}^{-1}$, $\varepsilon_{\text{lignin}}(\lambda)$, $\text{L mg}^{-1} \text{ cm}^{-1}$, and $\varepsilon_{\text{H}_2\text{O}_2}(\lambda)$, $\text{M}^{-1} \text{ cm}^{-1}$, the extinction coefficients at 254 nm for lignin and H_2O_2 , respectively, and z the depth of the irradiated solution, cm [21,22].

The OH radical's loss rates may be described as:

$$r_2^0 = k_{\text{H}_2\text{O}_2} \cdot [\text{H}_2\text{O}_2]_0 \cdot [\text{OH}^*]_{\text{qs}}, \quad (9)$$

$$r_3^0 = k_1 \cdot [\text{OH}^*]_{\text{qs}} \cdot \frac{[\text{lignin}]_0}{M_w}, \quad (10)$$

$$r_4^0 = k_{\text{HO}_2} \cdot [\text{OH}^*]_{\text{qs}} \cdot [\text{HO}_2^*]_{\text{qs}}, \quad (11)$$

$$r_5^0 = 2 \cdot k_{\text{OH}^*} \cdot [\text{OH}^*]_{\text{qs}}^2, \quad (12)$$

$$r_6^0 = k_{\text{H}_2\text{O}_2, \text{HO}_2^*} \cdot [\text{H}_2\text{O}_2]_0 \cdot [\text{HO}_2^*]_{\text{qs}} \quad (13)$$

Since the OH radical's concentration was very low compared to the lignin and hydrogen peroxide concentrations, it was considered to be quasi-stationary. Also the time of reaching quasi-stationary concentrations of the OH and HO_2 radicals was also short compared to the time characteristic for the initial changes in lignin or hydrogen peroxide concentrations. This assumption resulted in $r_1^0 = r_2^0 + r_3^0 + r_4^0 + r_5^0$ and $r_4^0 + r_6^0 = r_2^0$, in which r_4^0 and r_5^0 can be neglected due to their low values, and the OH radical's concentration can be obtained as follows:

$$[\text{OH}]_{\text{qs}} = \frac{2 \cdot k_{\text{a}, \text{H}_2\text{O}_2}(\lambda) \Phi_{\text{OH}}(\lambda) [\text{H}_2\text{O}_2]_0}{(k_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2]_0 + k_1 \cdot [\text{lignin}]_0 / M_w)} \quad (14)$$

In model, the expression $[1 - 10^{-(\varepsilon_{\text{lignin}}(\lambda) \cdot [\text{lignin}] + \varepsilon_{\text{H}_2\text{O}_2}(\lambda) \cdot [\text{H}_2\text{O}_2]) \cdot z}]$ was close to unity due to the high light absorbance by the compounds, $k_{\text{H}_2\text{O}_2}$, k_{OH^*} , k_{HO_2} , and $k_{\text{H}_2\text{O}_2, \text{HO}_2^*}$ were assumed to equal 3×10^7 , 5.2×10^9 , 7.1×10^9 , and $3.7 \text{ M}^{-1} \text{ s}^{-1}$, respectively [23,24], E_p^0 was measured to be $4.9 \times 10^{-6} \text{ mEinstein cm}^{-2} \text{ s}^{-1}$, z was 1.6 cm. Extinction coefficients of H_2O_2 , $\varepsilon_{\text{H}_2\text{O}_2}(254) = 12.8 \text{ M}^{-1} \text{ cm}^{-1}$, and lignin, $\varepsilon_{\text{lignin}}(254) = 0.019 \text{ L mg}^{-1} \text{ cm}^{-1}$, were determined using several dilutions of these substances in distilled water.

Since the lignin oxidation rate in UV/ H_2O_2 is the first order reaction on the lignin concentration at the conditions under consideration (Fig. 1), the initial lignin oxidation rate in the H_2O_2 /

UV-system was modelled by the second order equation dependent on the OH radical's concentration:

$$-\left(\frac{d[\text{lignin}]}{dt}\right)_0 = k_1 [\text{OH}]_{\text{qs}} [\text{lignin}]_0, \quad (15)$$

Using Eqs. (8), (14) and (15), the constant k_1 of OH radical reaction rate with “lignin-like” compounds was determined from the fit of experimental data of the initial lignin oxidation rate dependent on the initial hydrogen peroxide concentration at initial lignin concentration of 340 mg L^{-1} (Fig. 2). With this k_1 was determined as $1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ or $43 \text{ L mg}^{-1} \text{ s}^{-1}$. At high $[\text{H}_2\text{O}_2]_0$ the quasi-stationary concentration of OH radicals may be approximated by the following equation:

$$[\text{OH}]_{\text{qs}} = \frac{2 \cdot k_{\text{a}, \text{H}_2\text{O}_2}(\lambda) \Phi_{\text{OH}}(\lambda) [\text{H}_2\text{O}_2]_0}{k_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2]_0} = \frac{2 \cdot k_{\text{a}, \text{H}_2\text{O}_2}(\lambda) \Phi_{\text{OH}}(\lambda)}{k_{\text{H}_2\text{O}_2}}, \quad (16)$$

which resulted in the same value of k_1 (Fig. 2).

From the data obtained the reaction rates and radicals concentration may be estimated. For example, at $[\text{H}_2\text{O}_2]_0 = 1 \text{ M}$ the initial rate of OH radicals production as a result of light absorption is $r_1^0 = 4 \times 10^{-6} \text{ M s}^{-1}$, $[\text{OH}]_{\text{qs}} \approx 10^{-13} \text{ M}$, $[\text{HO}_2^*]_{\text{qs}} \approx 10^{-8} \text{ M}$, $r_2^0 = 3 \times 10^{-6}$, $r_3^0 = 1.5 \times 10^{-9}$, $r_4^0 = 7 \times 10^{-12}$, $r_5^0 = 7 \times 10^{-16} \text{ M s}^{-1}$, which shows that reaction rates r_4^0 and r_5^0 were correctly neglected and the quasi-stationary approximation for the changes in radical's concentration was also applicable. The interaction of lignin molecules with OH radicals was the slowest stage under the studied conditions limiting the overall lignin oxidation rate.

The dependences of lignin oxidation rate and lignin mineralization degree on initial hydrogen concentration presented in Fig. 2 had a maximum at $[\text{H}_2\text{O}_2]_0 = 0.25 \text{ M}$, above which the oxidation rate decreased due to the competitive reaction of OH radicals with hydrogen peroxide as was shown above.

To estimate the role of the diffusion factors, the diffusion rate constant k_D for reaction (3) was calculated using Eq. (17):

$$k_D = \frac{2}{3} \cdot \frac{k_B \cdot T \cdot N_A}{\eta} \cdot \frac{(r_{\text{lignin}} + r_{\text{OH}^*})^2}{r_{\text{lignin}} \cdot r_{\text{OH}^*}} \approx \frac{2}{3} \cdot \frac{k_B \cdot T \cdot N_A}{\eta} \cdot \frac{r_{\text{lignin}}}{r_{\text{OH}^*}}, \quad (17)$$

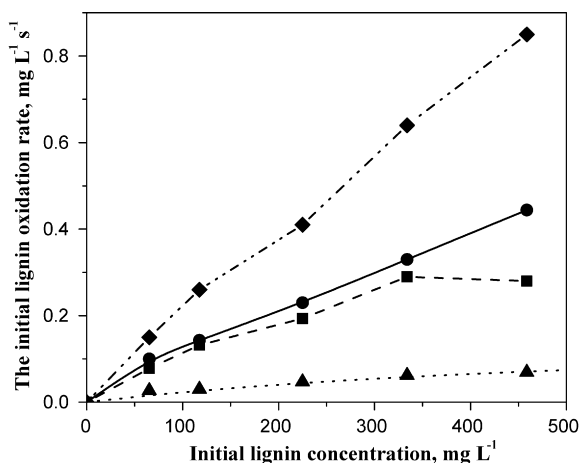


Fig. 1. Initial lignin oxidation rate vs. initial lignin concentration in different oxidation systems: initial hydrogen peroxide concentration 1 M, 25 °C, (▲) H_2O_2 /UV, pH 4.0, (◆) 5 mM $\text{Fe}(\text{NO}_3)_3/\text{H}_2\text{O}_2$, pH 2.5, (■) 16 g L^{-1} FeZSM-5/ H_2O_2 , pH 4.0, (●) 16 g L^{-1} FeZSM-5/ H_2O_2 /UV, pH 4.0.

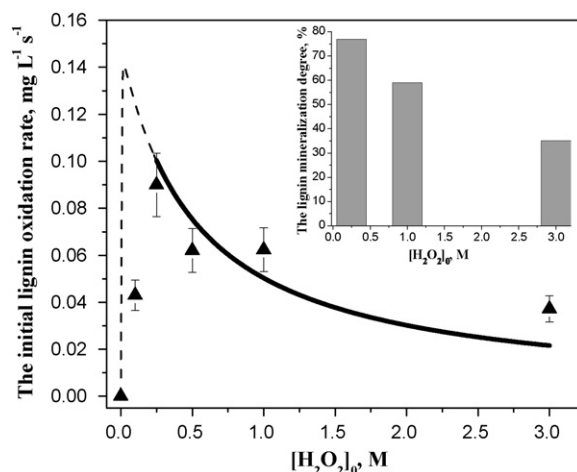


Fig. 2. Initial lignin oxidation rate vs. initial hydrogen peroxide concentration in the UV/ H_2O_2 system: (▲) Experimental data, dashed line—the fit of Eq. (15) using Eqs. (8) and (14); wide solid line—the fit of Eq. (15) using Eqs. (8) and (16). The inset shows the dependence of lignin mineralization degree on initial hydrogen peroxide concentration in 5 h of the reaction: initial lignin concentration 340 mg L^{-1} , pH 4.0, 25 °C.

where k_B is the Boltzmann constant, $1.381 \times 10^{-23} \text{ J K}^{-1}$, N_A the Avogadro constant, $6.02 \times 10^{23} \text{ mol}^{-1}$, η the solution viscosity taken as of water at 25°C , $0.9 \times 10^{-3} \text{ Pa s}$, T the solution temperature, K , r_{lignin} and r_{OH} the lignin and OH radical radii, respectively. Assuming by the molecular structure that $r_{\text{lignin}}/r_{\text{OH}} \approx 30$, the diffusion rate constant of OH radicals k_D was estimated as $10^{12} \text{ M}^{-1} \text{ s}^{-1}$, which is three orders of magnitude higher than k_1 . This shows clearly that the apparent reaction rate constant determined experimentally was limited by the kinetics of the reaction of OH radicals with lignin, not the diffusion of OH radicals in water.

The dependence of the lignin mineralization degree, i.e. its conversion to carbon dioxide and water, on pH with UV/ H_2O_2 is shown in Fig. 3 as a result of 5 h of treatment. Maximum lignin mineralization, about 80%, was observed at $[\text{H}_2\text{O}_2]_0 = 0.25 \text{ M}$ within wide range of pH from 4 to 8. At higher hydrogen peroxide concentration the lignin mineralization degree decreased due to the above-mentioned competitive reaction of OH radicals with hydrogen peroxide. In alkaline solution, at pH 10.0 a minor decrease in lignin mineralization was observed, which may be explained by the OH radicals scavenging by carbonate ions, present in such solutions. The decreased lignin mineralization in acidic media at pH 3.0 is possibly due to the lignin molecule protonation, which may inhibit oxidation by OH radicals.

3.2. Lignin adsorption on FeZSM-5

Lignin adsorption on the zeolite FeZSM-5 in aqueous suspensions strongly depended on pH (Fig. 4): at pH 3.0 lignin adsorption isotherm can be approximated by Langmuir model, when the adsorbent surface is covered with the lignin molecules monolayer:

$$a = \frac{K \cdot C_{\text{eq}} \cdot a_{\text{max}}}{1 + K \cdot C_{\text{eq}}}, \quad (18)$$

where C_{eq} is the lignin equilibrium concentration in solution, mg L^{-1} , K adsorption constant, L g^{-1} , a_{max} and a the maximum adsorption monolayer capacity of the zeolite and the surface concentration of lignin on zeolite respectively, $\text{mg}_{\text{lignin}} \text{g}_{\text{zeolite}}^{-1}$.

The experimental data fitted to the Langmuir model (Eq. (18)) gave the lignin adsorption constant $K = 46 \text{ L g}^{-1}$, and the lignin monolayer capacity of the FeZSM-5 $a_{\text{max}} = 3.5 \text{ mg}_{\text{lignin}} \text{g}_{\text{zeolite}}^{-1}$. Assuming the lignin molecular diameter to be about 20 nm, one can evaluate the surface area occupied by the lignin monolayer to

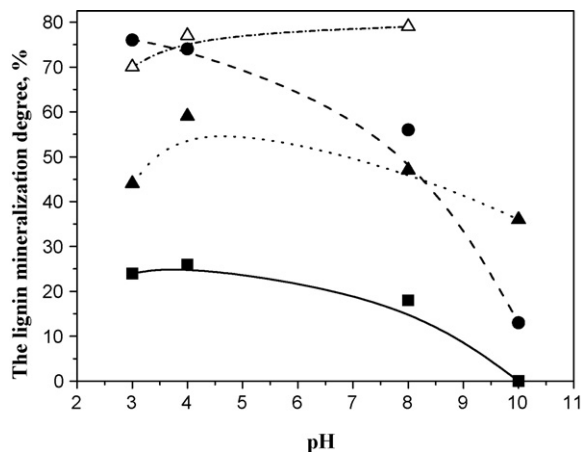


Fig. 3. The dependence of lignin mineralization degree on initial pH: treatment time 5 h, initial lignin concentration 340 mg L^{-1} , 25°C , (\blacktriangle) $1 \text{ M H}_2\text{O}_2/\text{UV}$, (\triangle) $0.25 \text{ M H}_2\text{O}_2/\text{UV}$, (\blacksquare) $16 \text{ g L}^{-1} \text{ FeZSM-5}/1.0 \text{ M H}_2\text{O}_2$, (\bullet) $16 \text{ g L}^{-1} \text{ FeZSM-5}/1.0 \text{ M H}_2\text{O}_2/\text{UV}$.

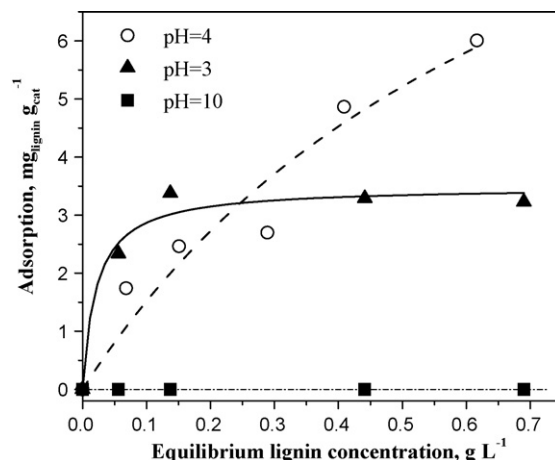


Fig. 4. Lignin adsorption isotherms on FeZSM-5 in aqueous suspensions at 25°C at different pH: symbols, experimental data; solid line, Langmuir model, Eq. (17).

be several tens of $\text{m}^2 \text{ g}^{-1}$, which is close to the external zeolite surface of around $53 \text{ m}^2 \text{ g}^{-1}$ (see Section 2.1).

At pH 4.0 the polylayer adsorption of lignin was observed exceeding monolayer capacity (Fig. 4). This may be explained by the tendency of lignin molecules to coagulate at pH value of 4.0–4.5, corresponding to the lignin isoelectric point [25]. No lignin adsorption on the zeolite surface was observed in alkaline solutions due to a negative charge of both zeolite FeZSM-5 surface, which was observed at any pH above 1.3 [26], and lignin- OH^- clusters. Similar behaviour of phenolic compounds adsorbed by aluminosilicates with a maximum adsorption at pH 4.5 was observed by Diez et al. [27].

3.3. Water delignification in homogeneous and heterogeneous Fenton systems

Earlier we have shown that for the organic substrates of low-molecular weight, such as 1,1-dimethylhydrazine and ethanol, the oxidation rate and the substrate mineralization degree in the heterogeneous Fenton system FeZSM-5/ H_2O_2 exceeded those in the homogeneous one [12,13], resulting in a more effective use of hydrogen peroxide. This was possibly due to the adsorption of organic substrates on the zeolite surface enhancing the adsorbed substrate interaction with OH radicals formed on the iron-containing catalytic sites also at zeolite surface. Principally different behaviour of Fenton oxidation systems was observed with aqueous solutions of high-molecular lignin: lignin oxidation turned out to proceed slower and with lower mineralization degrees in the heterogeneous system FeZSM-5/ H_2O_2 than in the homogeneous one (Fig. 5): the lignin mineralization degree, for example, at the initial H_2O_2 concentration 1 M and initial lignin concentration 340 mg L^{-1} in 5 h of treatment was 25 and 64% for heterogeneous and homogeneous systems, respectively. For both systems, the inhibition of the lignin oxidation rate when exceeding the H_2O_2 concentration of 1 M was observed (Fig. 5).

The low efficiency of the heterogeneous Fenton system may be explained by the several hypothetical reasons. Firstly, the medium diffusion distance of active OH radicals formed on the zeolite surface was found not to exceed 6 nm in water [28], while the thickness of the adsorbed lignin layer on the surface was not less than 20 nm. Thus, the lignin oxidation can proceed only in the reaction zone a few times shorter than the lignin molecule size. This may noticeably obstruct the lignin molecule oxidation with OH radicals due to the following reason. It is known that carboxylic functional groups have stronger affinity towards the zeolite

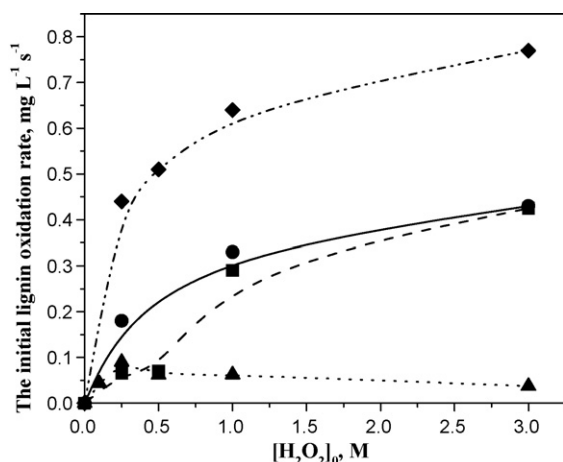


Fig. 5. Initial lignin oxidation rate vs. initial hydrogen peroxide concentration in different oxidation systems: initial lignin concentration 340 mg L⁻¹, 25 °C, (▲) H₂O₂/UV, pH 4.0, (◆) 5 mM Fe(NO₃)₃/H₂O₂, pH 2.5, (■) 16 g L⁻¹ FeZSM-5/H₂O₂, pH 4.0, (●) 16 g L⁻¹ FeZSM-5/H₂O₂/UV, pH 4.0.

surface as compared to hydroxylic groups [29,30]. As a result, the partially oxidised lignin products with carboxylic groups attached to the zeolite surface may form a “cage” in the catalyst surface vicinity creating steric obstacles for OH radical diffusion; these obstacles may result in OH radical’s preferential recombination instead of lignin oxidation. Secondly, assuming that desorption of oxidation products from the catalyst surface was the rate limiting stage, the rate of undesirable reaction of OH radicals with small-size hydrogen peroxide in zeolite surface vicinity would also favourably increase compared to the reaction with spacious lignin fragments. Thirdly, a similar tendency would appear if the adsorbed lignin had a lower reactivity towards OH radicals compared to free dissolved lignin molecules. Similar phenomenon was observed previously in oxidation of chlorinated organic substances by hydrogen peroxide in presence of activated carbon: OH radicals successfully oxidised free organic molecules, while the molecules adsorbed on the carbon surface were non-reactive [31].

Since homogeneous Fenton system acted only in acidic solutions and no oxidation proceeds in this system in neutral or alkaline media, the effect of pH on the lignin mineralization degree was studied only for the heterogeneous Fenton system (Fig. 3). For initial oxidant concentration of 1.0 M and initial lignin concentration of 340 mg L⁻¹ the deepest lignin mineralization of 25% was reached under acidic conditions, pH 3–4. In slightly alkaline solutions, pH 8.0, the initial oxidation rate decreased from 0.06 to 0.026 mg L⁻¹ s⁻¹ at the same initial concentrations. At pH 10.0 no lignin oxidation was observed, just as it was for the low-molecular weight substrates [13].

Besides of the adsorption features contribution to the catalytic activity of the zeolite described above, different behaviour of the zeolite Fenton system in acidic and alkaline solutions may be explained by two different mechanisms of hydrogen peroxide decomposition dependent on pH. In acidic and neutral media

H₂O₂ is decomposed most probably by free-radical way with formation of oxidant particles accessible for organic molecules, while in strong alkaline medium H₂O₂ decomposes on zeolite iron sites without formation of OH radicals, the phenomenon being observed in our earlier experiments, when the activation energy of H₂O₂ decomposition in acidic media, 50 kJ mol⁻¹, exceeds nearly three times the one in alkaline solution, 17 kJ mol⁻¹, with no catalytic oxidation of organic molecules by H₂O₂ in alkaline solutions [13].

It should be noted that although the initial lignin oxidation rate in the UV/H₂O₂ system was lower than in the Fenton reactions (Fig. 5), the lignin mineralization in 5 h of treatment was more effective in the first system (Fig. 3). The fact that in Fenton reactions without UV light the reaction practically stopped in 1 h was observed, whereas in the photo-assisted experiments the lignin oxidation rate did not change noticeably within 5 h of treatment thus resulting in deeper lignin oxidation.

3.4. Water delignification by photo-assisted heterogeneous Fenton system

Additive effect of the reaction rate in a combination of the heterogeneous Fenton with UV light, i.e. FeZSM-5/H₂O₂/UV system, when it reached the sum of the oxidation rates in separate FeZSM-5/H₂O₂ and H₂O₂/UV systems, was observed only at the H₂O₂ to lignin weight ratio not exceeding 100 (Fig. 5). At higher oxidant to substrate ratio the contribution of photolytic oxidation became negligible, making the catalytic reaction to dominate. The oxidation rate in FeZSM-5/H₂O₂/UV system also depended on pH (Fig. 3): if at pH 3.0 lignin mineralization in FeZSM-5/H₂O₂, H₂O₂/UV and FeZSM-5/H₂O₂/UV systems achieved 24, 44 and 76%, respectively, indicating more effective lignin oxidation in the photo-assisted heterogeneous Fenton reactions, then, on the contrary, in alkaline solutions the presence of zeolite resulted in greater inhibition effect in lignin oxidation compared to its photolytic oxidation (Fig. 3). This was due to above-mentioned difference in hydrogen peroxide decomposition in acidic and alkaline media in the FeZSM-5 presence [13]. Poor adsorption of lignin on zeolite in alkaline media also contributed to its poor catalytic oxidation (Fig. 4). Thus, the combination of FeZSM-5/H₂O₂ with UV light in alkaline solutions resulted in a faster hydrogen peroxide predominantly non-radical decomposition and in a lower lignin mineralization degree compared to H₂O₂/UV system.

Optimum conditions for the most effective water delignification for each of the studied AOPs are drawn together in Table 1. The non-catalytic photo-assisted lignin oxidation by hydrogen peroxide appears to be the most effective process for water delignification among the ones under consideration: the conversion degree of 97% was observed in a wide pH range at the lowest hydrogen peroxide consumption compared with Fenton systems.

3.5. Treatment of pulp-and-paper mill wastewater

The results of treatment of wastewater with FeZSM-5/H₂O₂, FeZSM-5/H₂O₂/UV and UV/H₂O₂ are shown in Table 2. The

Table 1

Treatment conditions for the most effective water delignification in different oxidation systems: initial lignin concentration 340 mg L⁻¹, treatment time 5 h, 25 °C

System	[H ₂ O ₂] ₀ (M)	pH ₀	Initial oxidation rate (mg L ⁻¹ s ⁻¹)	Lignin conversion degree (%)	Lignin mineralization degree (%)
5 mM Fe(NO ₃) ₃ /H ₂ O ₂	3	2.5	0.77	97	82
16 g L ⁻¹ FeZSM-5/H ₂ O ₂	3	3	0.22	66	35
16 g L ⁻¹ FeZSM-5/H ₂ O ₂ /UV	3	4	0.43	88	79
H ₂ O ₂ /UV	0.25	4–8	0.04	97	78

Table 2

Characteristics of the wastewater from pulp-and-paper mill after 7-h treatment by different oxidation methods at 25 °C

Treating system	[H ₂ O ₂] ₀ (M)	C _{lignin} (mg L ⁻¹)	COD (mg O ₂ L ⁻¹)	Turbidity (NTU)	Colour (degrees)	pH
None	0	48	313	100	514	7.6
16 g L ⁻¹ FeZSM-5	0	36	283	48	274	8.0
16 g L ⁻¹ FeZSM-5/UV	0	56	270	54	308	8.0
UV/H ₂ O ₂	0.1	7	64	70	258	8.3
16 g L ⁻¹ FeZSM-5/H ₂ O ₂	1	47	240	52	284	3.7 ^a
16 g L ⁻¹ FeZSM-5/H ₂ O ₂ /UV	1	27	170	16	78	3.9 ^a

^a HCl was added at the starting point of treatment.

adsorption of the pollutants of the zeolite surface, as expected, reduced the lignin content, COD, colour and turbidity with the slight increase in pH. The application of UV to the zeolite catalyst suspension resulted in somewhat increased lignin concentration and colour with simultaneous decrease in COD, which may be explained by the formation of coloured phenoxy-groups observed previously in [32,33].

The most effective lignin oxidation, for 85%, and pollutants' mineralization, 80%, were observed in the wastewater treatment with H₂O₂ at its 0.1 M concentration under UV-radiation at pH 8.3, which supports the observation made previously with lignin solutions.

Rather poor performance of heterogeneous Fenton system in delignification of the wastewater may be explained by the predominant oxidation of other wastewater constituents, which is seen in the decreased COD, colour and turbidity. Poor oxidation of lignin, observed earlier in solutions treated in heterogeneous Fenton system, being complicated with the presence of other admixtures thus found confirmation in these experiments.

The significant improvement of the heterogeneous Fenton reagent's performance was observed in UV-assisted reaction, although, similar to the experiments with synthetic solutions of lignin, the presence of FeZSM-5 resulted in drastic decrease in treatment efficiency compared to oxidation with H₂O₂/UV.

4. Conclusions

The adsorption of lignin on FeZSM-5 zeolite fits well to the Langmuir model at pH 3.0, the adsorption constant and the monolayer capacity were thus found. The efficiency of lignin heterogeneous Fenton oxidation on the FeZSM-5 catalyst surface appeared to be low due to, most probably, steric hindrance of large adsorbed lignin molecules oxidation with short space of OH radicals diffusion from the surface and partial deactivation of adsorbed lignin. Oxidation of lignin appeared to be more effective in homogeneous Fenton and hydrogen peroxide photolysis processes. The limiting stage of the overall lignin UV-assisted oxidation by hydrogen peroxide appeared to be the interaction of OH radicals with lignin molecule, the constant of which was determined and compared to the diffusion rate constant. The lignin oxidation in H₂O₂/UV system was found to be the most effective among studied delignification methods in terms of low optimum oxidant concentration, delignification and lignin mineralization over the wide range of pH. Under acidic media conditions, however, UV-assisted heterogeneous Fenton treatment showed the performance close to the one of H₂O₂/UV oxidation. The experiments with biologically treated pulp-and-paper mill wastewater containing lignin supported the findings made with lignin synthetic solutions.

Acknowledgements

This research was sponsored by the Academy of Finland "Russia in Flux" programme, Project No. 208134, Olga Makhotkina's IAESTE scholarships, the NATO SfP. Programme 981461, the President's Grant of Russia MK-907.2007.3 and the grant of the ISTC 3305.

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